

DNAPL Detection and Characterization Techniques

GeoTrans, Inc.



Presentation Overview

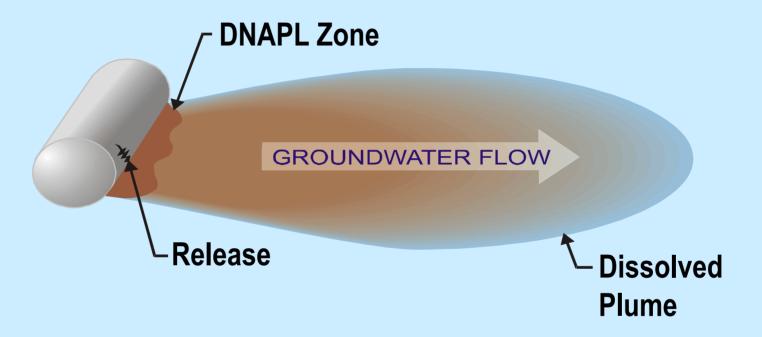
- Definitions
- Why is DNAPL an Issue?
- Regulatory History and Status
- Strategies for Detection and Characterization
- Tools for Characterization
 - Noninvasive
 - Invasive
- Summary

Definitions



- DNAPL Dense nonaqueous phase liquid
 - Chemicals with densities greater than that of water and aqueous solubilities that are (generally) low
 - Chlorinated solvents
 - Creosote/coal tar
 - PCBs
- DNAPL entry location; DNAPL zone (includes DNAPL, sorbed chemicals and diffused chemicals); dissolved contamination zone

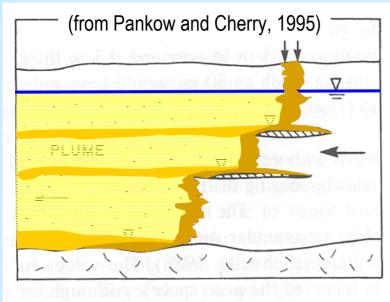
Conceptual Site Schematic

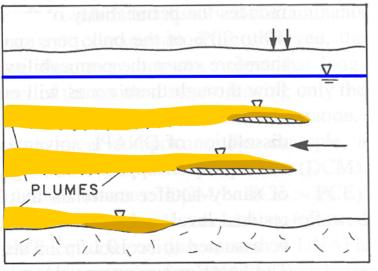


Forms of DNAPL

- Free-phase (mobile) DNAPL that is under positive pressure and can drain to a well
 - Could be currently moving or contained in a stratigraphic trap
- Residual DNAPL (discontinuous blobs and ganglia) that is held under capillary pressure (related to fluid interfacial tension) that will not drain to a well
 - Makes it difficult to find

DNAPL in Pools

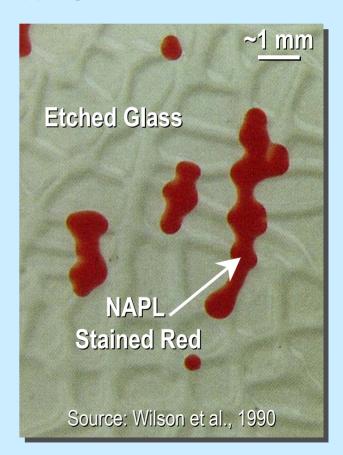




- Less contact with flowing groundwater than DNAPL at residual saturation
- Dissolution also limited by weak vertical dispersion
- Greater DNAPL volume in pools
- Thus, the rate of dissolution is reduced and the DNAPL lifetime is extended compared to where DNAPL is dispersed at residual saturation

DNAPL at Residual Saturation

- During migration, a significant portion of DNAPL is retained in porous media due to capillary trapping.
 - Vadose zone: 10% 20% typical
 - Saturated zone: 10% 50% typical
 - Field sampling volume problem
- DNAPL at residual saturation remains immobile unless it is replenished by new releases or subjected to increased hydraulic force.
- Because it will not flow to a well, DNAPL is difficult to detect.



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Why is DNAPL an Issue?

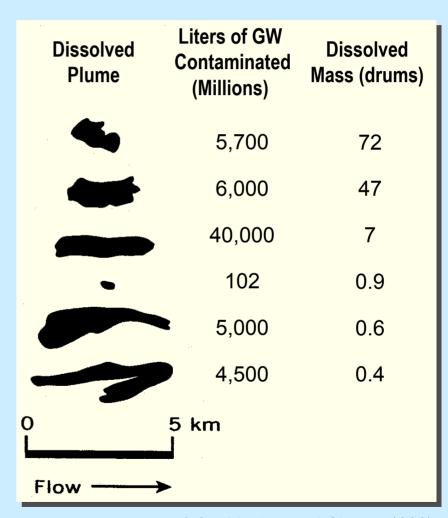
- Widespread production, transport, use, release, and disposal of DNAPLs, particularly chlorinated solvents
- Uses include military equipment manufacturing and maintenance, vapor degreasing operations, dry cleaning, and septic tank cleaners
- Potential for groundwater contamination high due to DNAPL chemical toxicity, persistence, and migration potential
- Chlorinated solvents among the most prevalent contaminants detected in groundwater supplies and at waste sites





Why is DNAPL an Issue? (cont.)

- Chemical solubilities much greater than MCLs (small DNAPL volume can produce large dissolved plume that does not readily degrade)
- DNAPL source difficult to locate and characterize
- DNAPL removal difficult and costly (complete removal may be impossible at most sites)
- No DNAPL site has been cleaned up to MCLs



(after Mackay and Cherry, 1989)

Why is DNAPL an Issue? High Potential for Groundwater Contamination

| DNAPL | Millions lbs made in U.S. 1990 | S.G. | Viscosity (cP) | Solubility (mg/L) | MCL (mg/L) | Ratio of Solubility to MCL |
|-----------|--------------------------------------|------|-------------------|----------------------|---------------|----------------------------|
| 1,2-DCA | 13,800 | 1.24 | 0.80 | 8,690 | 0.005 | 1,738,000 |
| 1,1,1-TCA | 802 | 1.34 | 0.83 | 1,360 | 0.200 | 6,800 |
| DCM | 461 | 1.33 | 0.43 | 20,000 | 0.005 | 4,000,000 |
| CTET | 413 | 1.59 | 0.97 | 800 | 0.005 | 160,000 |
| PCE | 372 | 1.62 | 0.89 | 150 | 0.005 | 30,000 |
| TCE | 165 | 1.46 | 0.57 | 1,100 | 0.005 | 220,000 |
| Water | | 1.00 | 1.00 | | | |

S.G. = specific gravity cP = centi-Poise

Chemical Safety Data Sheet SD-14

ADOPTED 1947

TRICHLOROETHYLENE



PROPERTIES

ESSENTIAL INFORMATION FOR SAFE HANDLING AND USE

TRICHLOROETHYLENE

WARNING! VOLATILE SOLVENT

Use with adequate ventilation.

Avoid prolonged or repeated breathing of vapor.

Avoid prolonged or repeated contact with skin.

Do not take internally.

7. WASTE DISPOSAL

7.1 Residue may be poured on dry sand, earth, or ashes at a safe distance from occupied areas and allowed to evaporate into the atmosphere.

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Regulatory History and Status

- Studies of pump-and-treat systems in the 1980s showed that suspected DNAPL sites were not being restored at predicted rates
- This led to the concept of Technical Impracticability (TI) waivers in 1993
 - U.S. EPA Directive 9234.2-25
- Since 1993, only about 50 TI waivers have been granted

Technical Impracticability

- "EPA expects ...all <u>reasonable</u> efforts will be made to identify the location of source areas through historical information searches and site characterization efforts."
- "appropriate level of effort for source removal..."
- "Even partial removal of contaminant sources..."

TI Waiver

- Characteristics of a TI waiver in 1999 (Region 9)
 - Creosote DNAPL, with high viscosity, is naturally contained in topographically low troughs on a shallow clay.
 - The downgradient dissolved plume is small and is biodegrading (plume is not expanding).
 - A review of remedial technologies indicated that no technology was capable of removing all DNAPL; therefore, it was technically impracticable to restore groundwater quality in the creosote DNAPL area.
 - Region 9 required submittal of a TI evaluation that strictly adhered to the EPA Guidance Document. Three submittals (an original and two revisions) were required before the TI waiver was granted (included approval by Headquarters).
 - Note: TI waivers are very dependent on the EPA Region and other nontechnical factors.

NFESC DNAPL Remediation Technologies Survey

Objective

 Collect information on the state of the science with regard to remediation of DNAPL source zones in groundwater

Benefits to Participants

- Access to final report containing:
 - Technology theory and application
 - Technology performance evaluation and development status
 - Remedial costs and technical practicability/impracticability
- Helping to expand the knowledge base and to identify potential new research areas
- List of technology experts and vendors generated from list of survey respondents

For information and to complete the survey: https://projects.geosyntec.com/navy_rocs/

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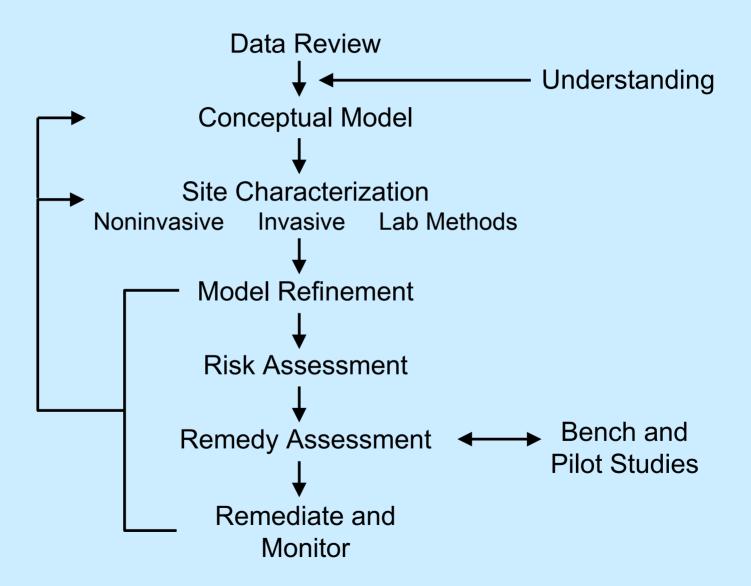
Strategies for DNAPL Detection and Characterization

- Develop realistic site conceptual model
 - Need to understand stratigraphy
- Use noninvasive information and minimal invasive methods first
- Use plume information to infer up hydraulic gradient source conditions
- Select source investigation methods that provide desired remediation data and minimize risk of mobilization

Basic DNAPL Characterization Questions

- Is DNAPL present?
- If so, where are the DNAPL sources (e.g., map locations, hydrogeologic units)?
- How long has the DNAPL been in the subsurface?
- What are the characteristics of the DNAPL sources that are important to remediation (e.g., quantity, form, architecture, physical and chemical attributes)?

Phased Site Management



Presentation Overview

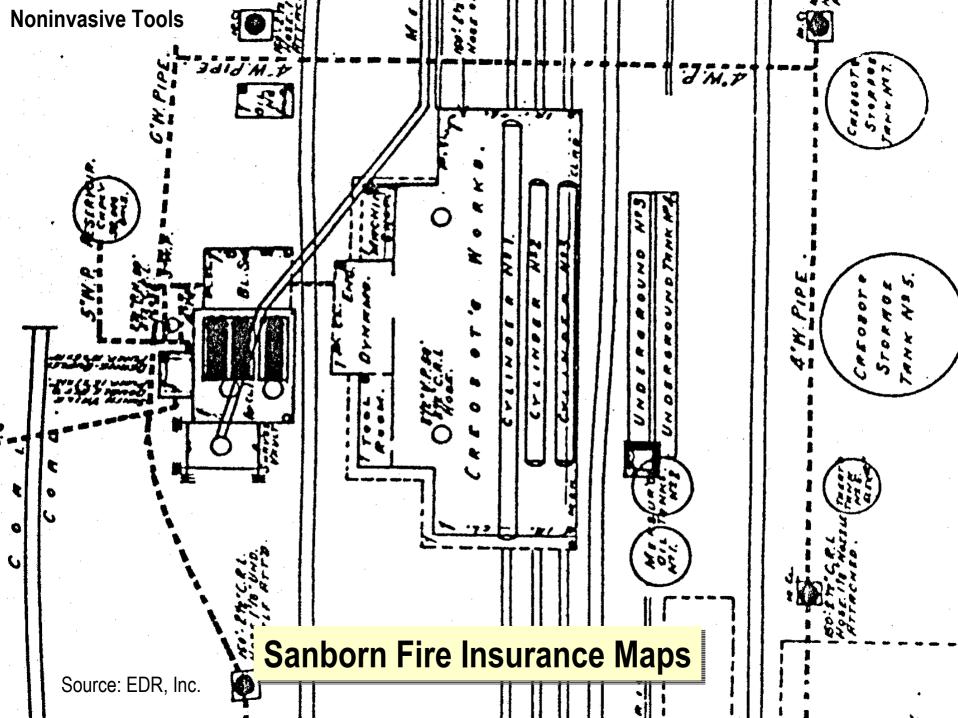
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Noninvasive Tools for DNAPL Characterization

Site history information (e.g., chemical use, inventory and disposal records)

- Historical aerial photographs
- Geologic fractures/outcrops
- Soil gas analysis
- Surface geophysics
- Site infrastructure information (e.g., sewers)
- Employee/witness interviews

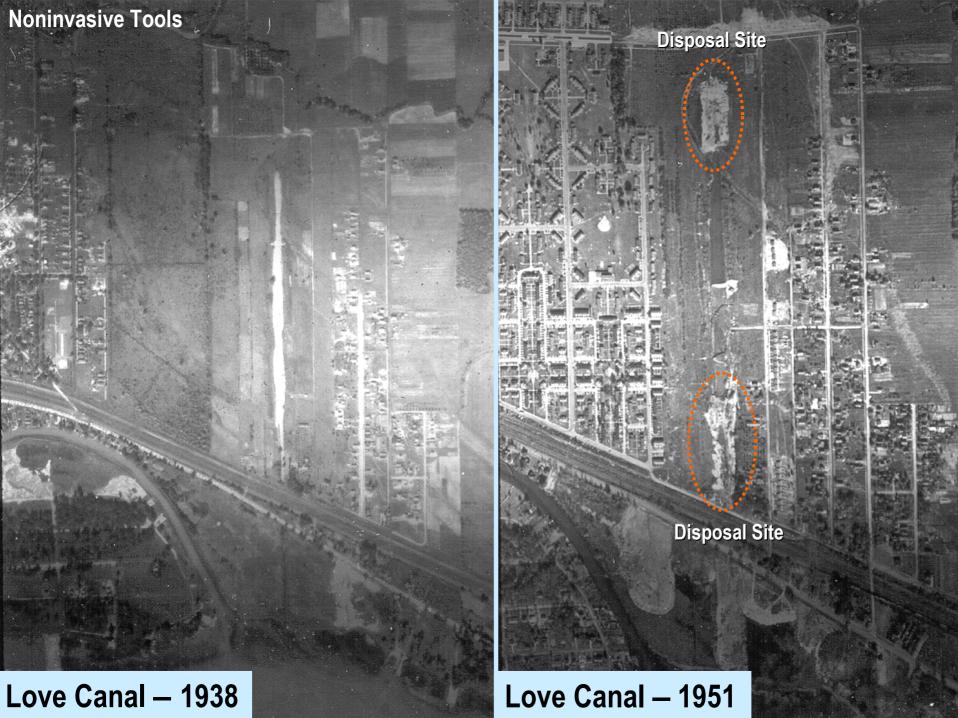


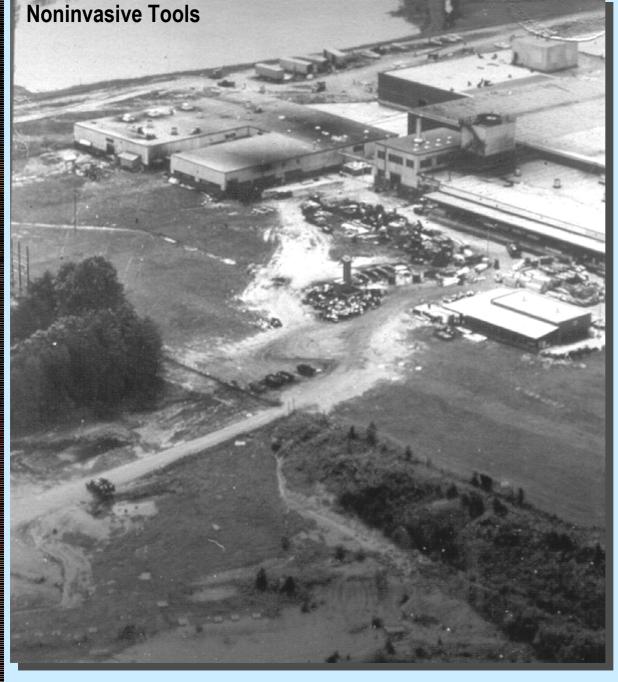


Aerial Photographs for Site Investigation

An inexpensive, noninvasive tool to assess . . .

- Historic site use and conditions
 - Source areas
 - Land use
 - Drainage
 - Vegetative stress
 - Surface contamination
 - Geology
 - Relate environmental data to historic site conditions
- Fracture trace analysis
 - Preferential pathway analysis
 - Well siting



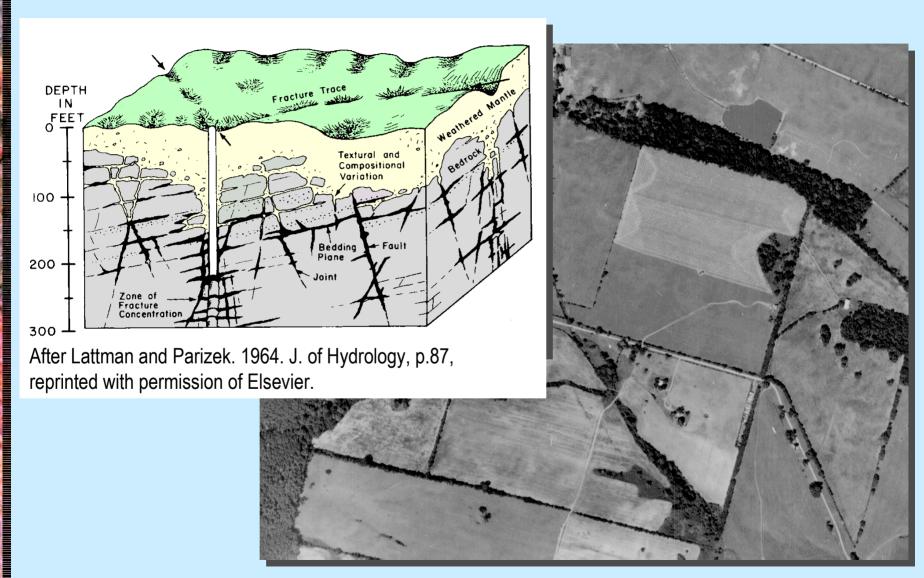


1966 oblique photo showing the rear end of a metal works facility where groundwater is contaminated by chlorinated solvents



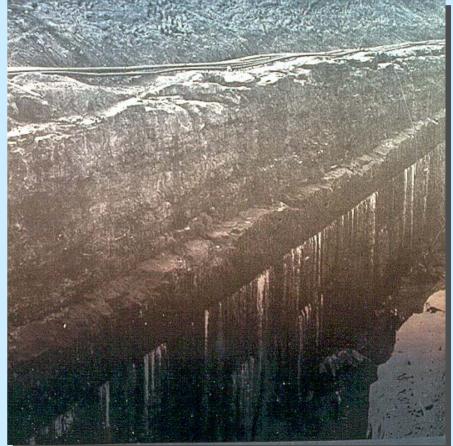
RITS Spring 2003: DNAPL Detection and Characterization Techniques

Fracture Trace Analysis





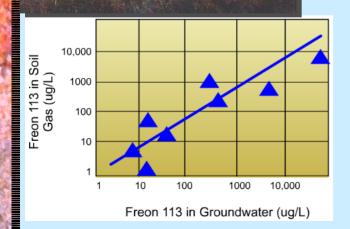
Vertical and Bedding Plane Fractures in the Lockport Dolomite Outcrop

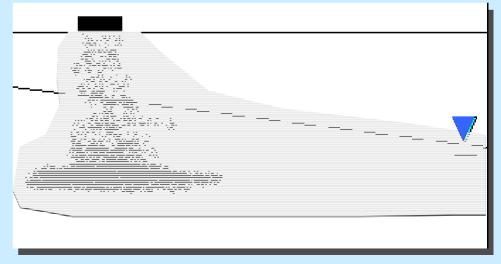


RITS Spring 2003: DNAPL Detection and Characterization Techniques



- Rapid delineation of volitile organic compompounds (VOCs) evolving from NAPL in the vadose zone (source areas)
- Delineate shallow GW contamination
- Less effective for deep GW contamination



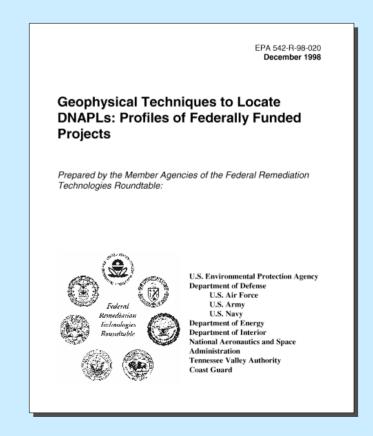


Soil-Gas Surveys (cont.)

- Older releases in hot environments (e.g., arid West) may have limited signal due to volatilization
- Can use passive soil-gas sampling, e.g., Gore-Sorber® (cost: \$125-225/sample + equipment cost of \$25-85/day + mob cost of \$200-600/day)
- Can use active soil-gas sampling (cost: \$110-190/sample)
- Phased approach: passive, active, vertical soil-gas monitoring (LaPlante, 2002) (DoD facility)

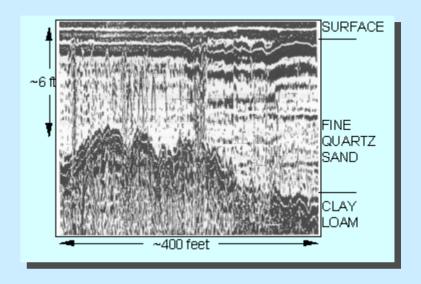
Surface Geophysical Surveys

- Conventional surface methods to delineate stratigraphy, buried metal, and conductive fluids
- Less widely used high resolution techniques
 - To delineate DNAPL traps
 - To infer DNAPL presence
- Methods subject to numerous interferences and interpretation errors

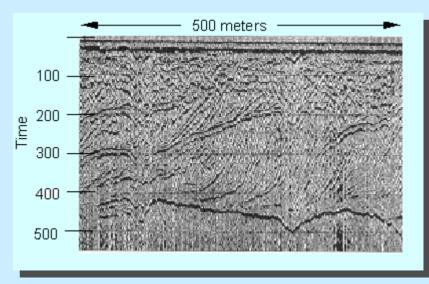


Ground-Penetrating Radar (GPR)

- Measures dielectric and conductivity properties by transmitting electromagnetic waves and recording their reflection
- Used to delineate stratigraphy, buried wastes, and utilities in cross section
- Penetration typically 6 to 30 feet bgs limited by increasing clay content, fluid content, and fluid conductivity







Noninvasive Tools

Electromagnetic (EM) Conductivity

- Measures bulk electrical conductance by recording changes in induced EM currents
- Used to infer presence of conductive contaminants, buried wastes, and stratigraphy

Station measurements, depth depends on

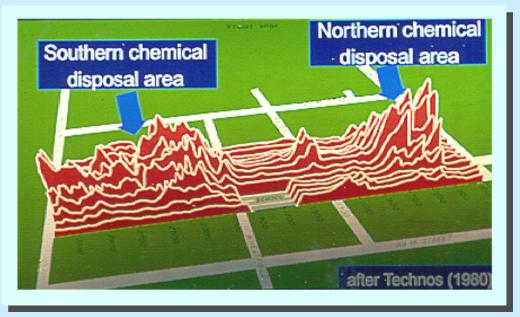
transmitter-receiver spacing



Source: Geonics, 1999

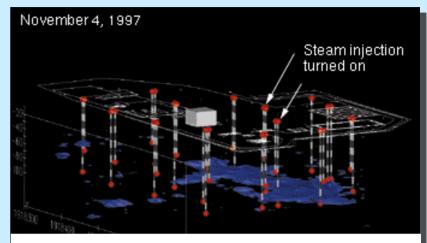


Source: Geonics, 1999

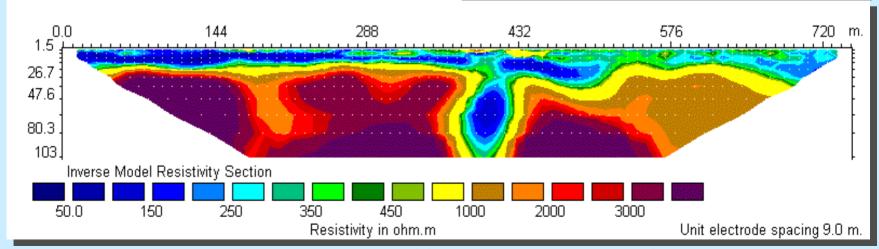


Electrical Resistivity

- Measures resistivity of subsurface including effects of soil type (clay content), bedrock fractures, contaminants, and groundwater
- Used to delineate stratigraphy, infer depth to water table, locate fractures and faults, identify karst features, etc.
- Electric resistance tomography (ERT), using cross-hole electrode arrays

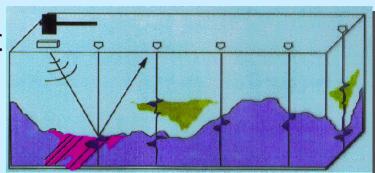


Resistivity increases used to track steam injection at Visalia, CA wood-treating site Source: SteamTech and www.llnl.gov

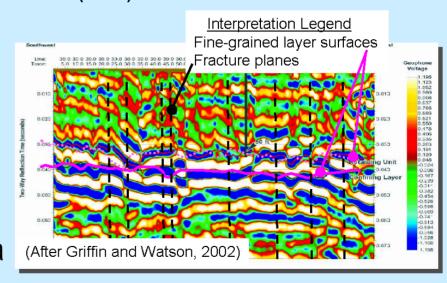


High-Resolution Seismic Reflection DoD / NFESC Demonstration (DoD, 10/99)

- Evaluate 3-D seismic reflection to detect DNAPL and delineate stratigraphy
- Acoustic energy reflects off strata interfaces (and DNAPL?)

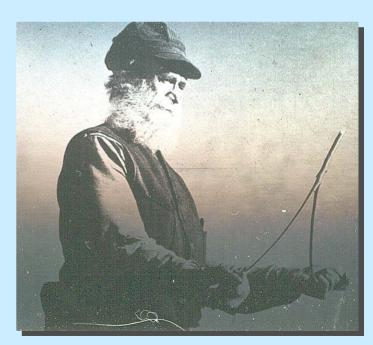


- Four test sites: Letterkenny Army Depot (PA), NAS Alameda (CA), Tinker AFB (OK), Allegany Ballistics Lab (WV)
- Confirmation sampling showed DNAPL at only 1 of 27 targets; successful target indistinguishable from other anomalies
- 3-D seismic surveys not effective at directly detecting DNAPL; potentially useful for imaging strata



Geophysical Methods – Limitations

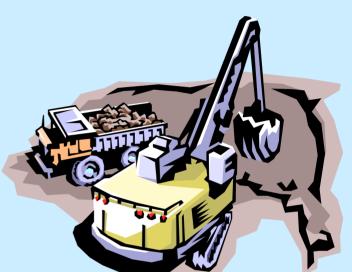
- Subsurface DNAPL is a poor target for geophysical methods
- Thus, direct detection of DNAPL is unlikely
- Geophysical methods are used to delineate stratigraphy, which may assist DNAPL delineation
- Changes in DNAPL saturation have been detected using geophysical methods during research studies
- Use of geophysical methods to attempt direct detection of NAPL has mainly been limited to research projects and government funded demonstration projects



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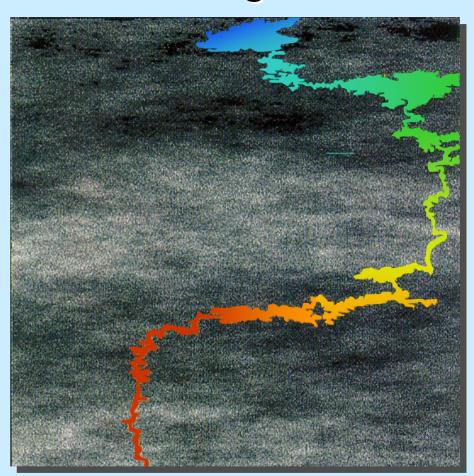
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- Soil Examination Methods
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- Organic vapor analysis (OVA)
- Ultraviolet (UV) fluorescence
- Hydrophobic dye shake test
- Ribbon NAPL Sampler (RNS) core strip test
- Chemical and partitioning analyses
- Downhole Methods
 - Membrane Interface Probe (MIP)
 - RNS (aka NAPL FLUTe)
 - Cone Penetrometer Technology (CPT)/Laser Induced Fluorescence (LIF)
- Groundwater Quality Profiling using Direct Push (DP) and Multilevel Wells
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DNAPL Delineation Challenges

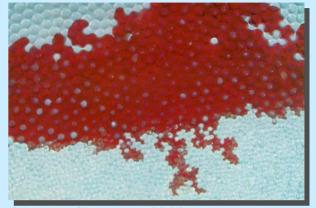
- Limited information about sources/releases
- Complex migration patterns
- Small volumes, which can create persistent dissolved plumes, are difficult to delineate
 "needle in haystack" problem
- Risk of mobilization by intrusive characterization activities



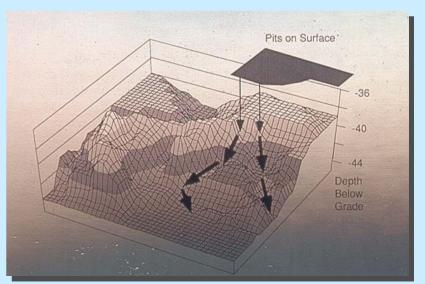
Source: Ewing, R.P. and B. Berkowitz, 1998 Reproduced by permission of AGU

Use Site Conceptual Model to Focus Investigation

- Effects of capillary pressure and gravity
- Stratigraphic barriers and traps
 - Is there a bottom to the site?
 - Organic layer absorbent (e.g., peat)?
- Migration pathways
 - Fractures in rock or cohesive soil
 - Coarse lenses and layers
 - Rootholes
 - Man-made structures (sewers, foundations, wells)
 - Heterogeneity and anisotropy
- Fine-grained diffusion sources



Source: Schwille, 1988
Reproduced by permission of CRC Press



Source: Newell and Connor, 1992

Invasive Characterization Method Goals

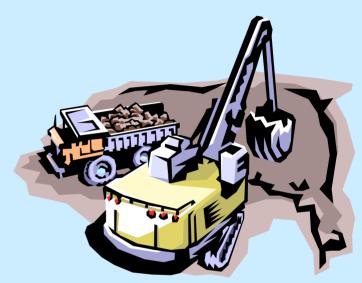
- Unambiguously identify DNAPLs in the subsurface
- Minimize investigation-derived waste (IDW)
- Eliminate undesirable gravitational movement of DNAPLs
- Provide cost savings



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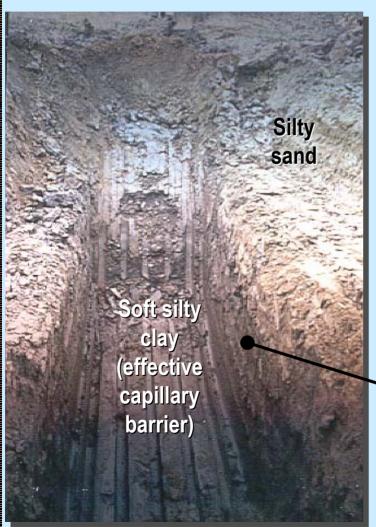
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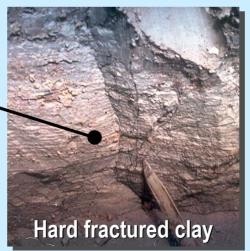
Test Pits

Used to define shallow soil stratigraphy, structure, and NAPL distribution



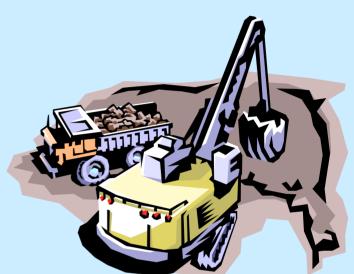


Love Canal site, Niagara Falls, NY





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DNAPL Characterization Using Soil Cores

- Continuous cored soil samples can help identify DNAPL presence and migration pathways
- Soil coring with direct push technology (i.e., Geoprobe®) is relatively inexpensive
- Use sample tube liners to minimize VOC losses
- A photoionization detector (PID) can be used to select "hot" portions of the soil core for sampling and preservation
- Perform soil sampling of suspected source areas using methanol as a preservative (EPA SW846 Method 5035)

Invasive Tools: Probing and Drilling

Benefits of Direct-Push Sampling

Rotary Hammer (Percussion) and Cone Penetration Units

- Rapid stratigraphic logging and contaminant detection using sensor systems
- Rapid, depth-discrete sampling of soil, soil gas, and water
- No drill cuttings, little IDW
- Minimally invasive; effective grouting and sealing capabilities
- Reduced potential for contaminant drag-down
- Standard methods
 - Direct-push soil sampling (ASTM D-6282)
 - Direct-push groundwater sampling (ASTM D-6001)
 - Cone penetration testing (ASTM D-3441)

Invasive Tools: Probing and Drilling

Geoprobe® and Cone Penetration Tools

- Soil gas sampler
- Soil sampler
- Groundwater sampler
- CPT stratigraphy
- Soil moisture probe
- Electrical conductivity/resistivity
- Fluorescence detector
- Downhole camera
- MIP and thermal desorption VOC sampler
- Permeability
- Grouting module



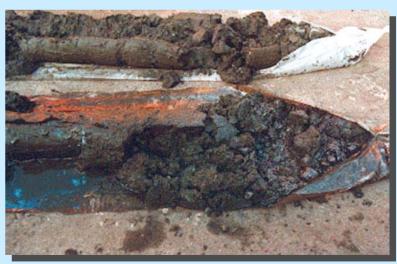
Comparison of Direct Push Methods

| Technique | Advantage | Limitation |
|--------------------------------------|---|---|
| Percussion Probing (Geoprobe®) | Less expensive More mobile and available Well-developed sampling tools Availability of certain sensors | Difficult to penetrate hard/dense soilsDepth limitation |
| Cone Penetration | Greater depth penetration Certain sensors better developed (LIF, tip resistance, sleeve friction, etc.) | More expensive Less available Less maneuverable |

Rotasonic Drilling

- Employs use of high-frequency mechanical vibration and limited rotary power to drill
- Can provide excellent quality, large diameter, relatively undisturbed core of soil and rock for characterization
- Maximizes core volume, minimizes other IDW
- Contaminant drag-down a concern; (reduce risk by drilling through isolation casing)
- Fast
- Limited availability and high cost





Photos courtesy of Sonic Drill Corp.

Drilling at DNAPL Sites



DNAPL on Lockport Dolomite

Hyde Park Landfill Site,

Niagara Falls, NY

- All methods present some risk of dragdown and mobilization
- Many precautions can be taken to limit risk
 - Outside-in
 - Carefully examine samples and screening data
 - Telescope
 - Use direct push
 - Control hydraulic pressure in hole
 - Minimize open-hole length and duration
 - Stay shallow, monitor deep downgradient

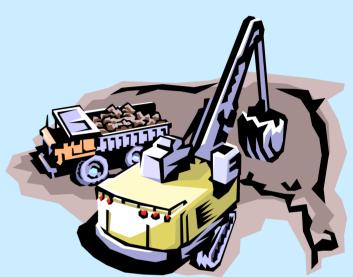
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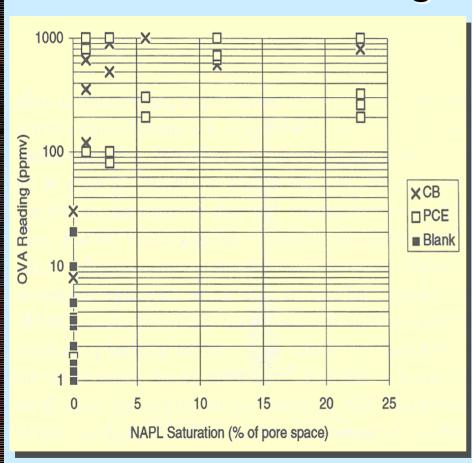
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Invasive Tools: Soil Examination Methods

Organic Vapor Analysis Screening of Soil Cores



Sample headspace experiment results

Source: Cohen et al., 1992

- Rapid and inexpensive
- High concentrations of VOCs associated with NAPL presence
- Useful to focus sampling
- Readings sensitive to effective contaminant volatility, water content, sample temperature, and sample handling



OVA screening of soil core

Source: Griffin and Watson, 2002b

UV Fluorescence

- Common chlorinated solvents generally <u>do not</u> <u>fluoresce</u> unless mixed with fluorescent impurities:
 - Oil and grease removed by solvent in degreasing operations
 - Petroleum products encountered in the subsurface
 - Humic compounds from natural organic matter
- Coal tar and creosote DNAPLs fluoresce
- Naturally occurring fluorophores (e.g., calcium carbonate shell fragments in coastal plain sediments) can confound use of fluorescence as a contaminant detection tool



Coal tar fluorescence in soil core

UV Fluorescence Detection Methods

Advantages

- Quick and inexpensive
- Many NAPLs fluoresce
- Can provide detailed information on relationship between stratigraphy and contaminant distribution
- Can document using a digital camera

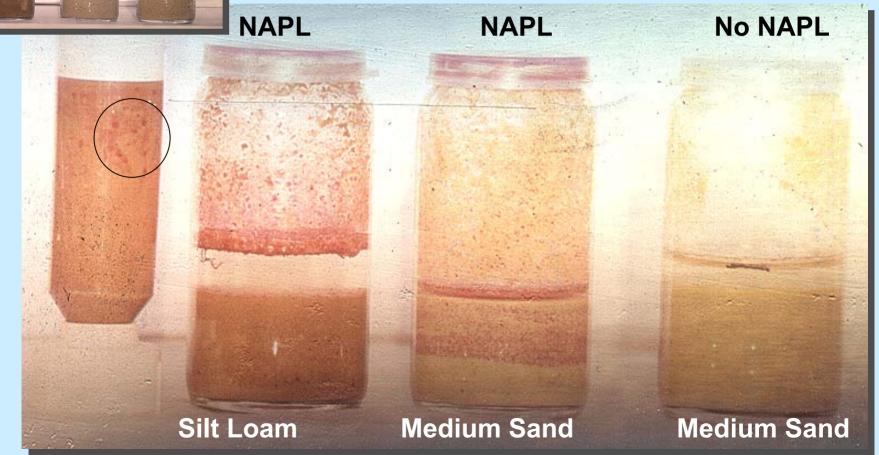
Limitations

- Requires fluorescent NAPL
- Indiscriminate
- Interference from non-target fluorescent materials (such as shell fragments in coastal sediment)
- Significant potential for false positives and false negatives

Known background and NAPL-contaminated samples should be checked for interference and site-specific NAPL response

Hydrophobic Dye Shake Test

Mix soil sample with water and a tiny amount of hydrophobic dye powder (e.g., Sudan IV)



Hydrophobic Dye Shake Test Use and Limitations

- Known background and NAPL-contaminated samples should be examined to check for interference and sitespecific response
- Can only detect NAPL if present in sample
- Potential for false positives (reaction with other organic matter) and false negatives (not enough NAPL present)
- Visual contrast can be difficult to discern in dark soil

Using a Ribbon NAPL Sampler (RNS) (aka NAPL FLUTe™) to Detect NAPL in Soil Core

- The RNS, developed for downhole emplacement, can be used to find NAPL in rotasonic drill soil core samples
- The RNS cover is a hydrophobic dye-striped tubular fabric designed to contact soil core extruded from a barrel
- NAPL that contacts the RNS will react with its dye and produce a visible stain on the outside of the cover
- The core bag can be photographed, manipulated to increase soil contact with the reactive fabric, and slit open for vapor analysis and sampling

Source: www.flut.com

Invasive Tools: Soil Examination Methods

RNS Usage







Invasive Tools:
Soil Examination Methods

Example Results Using Dye Strips

SB-6 at 45.5 ft bgs

Visual: ND

UV: ND

Dye Shake Test: ND

OVA: 3,000 ppm

Analysis: 0.065 mg/kg Freon 113

SB-14 at 54 ft bgs

Visual: ND

UV: ND

Dye Shake Test: ND

OVA: >5,000 ppm

Analysis: 680 mg/kg Freon 113





Note: Freon 113 concentration >84 mg/kg suggests NAPL presence

Using RNS Strips to Detect NAPL in Soil Core

Advantages

- Relatively simple, direct, and cost-effective (~\$4/ft for hydrophobic dyeimpregnated cover)
- Can provide detailed information on relationship between stratigraphy and contaminant distribution
- Amenable to rapid documentation via photography

Limitations

- Minor discoloration of liner associated with handling and contact with plastic core sleeves
- Relatively faint reaction to some NAPLs
- Color fading and/or nondetection due to evaporation
- Wicking may exaggerate NAPL presence
- Potential for false positives and false negatives

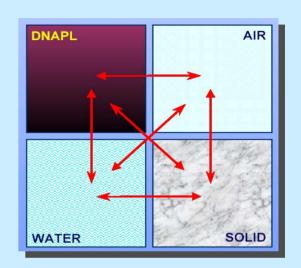
Chemical Analysis of Soil Core Samples

- Collect the soil sample with preservation
- Analyze the extract (preservative) and back-calculate soil concentrations
- Use soil concentrations to determine the DNAPL saturation in the soil and more

Invasive Tools: Soil Examination Methods

Calculating DNAPL Saturation in Soil Based on Chemical Analysis and Equilibrium Partitioning Calculation

- Feenstra et al. (1991)
 - Assesses presence of NAPL
- Mott (1995): SOILCALC
 - Assesses presence of NAPL
 - Estimates NAPL composition
- Mariner et al. (1997): NAPLANAL calculates:
 - NAPL saturation
 - NAPL composition
 - VOC concentrations in each phase
 - NAPL composition and volume in water-NAPL emulsions (♣ = 0)



Mass of i = sum of mass of I in all phases:

$$\rho_{t}C_{t}^{i} = \phi_{w}C_{w}^{i} + \phi_{a}C_{a}^{i} + \phi_{n}C_{n}^{i} + \phi_{ss}C_{s}^{i}$$

Total density = weighted average of all densities:

$$\rho_t = \phi_w \rho_w + \phi_a \rho_a + \phi_n \rho_n + \phi_s \rho_s$$

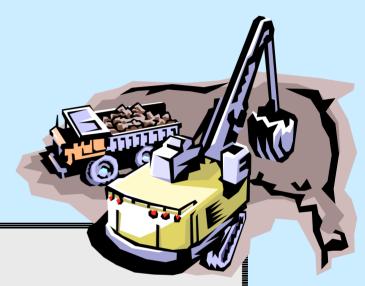
Source: Duke Engineering and Services, 1998

NAPLANAL available at www.dnapl.com/publications.html

- Test Pits
- Probing and Drilling
- Soil Examination Methods
- Invasive Tools for DNAPL Characterization
- Organic vapor analysis (OVA)
- Ultraviolet (UV) fluorescence
- Hydrophobic dye shake test
- Ribbon NAPL Sampler (RNS) core strip test
- Chemical and partitioning analyses

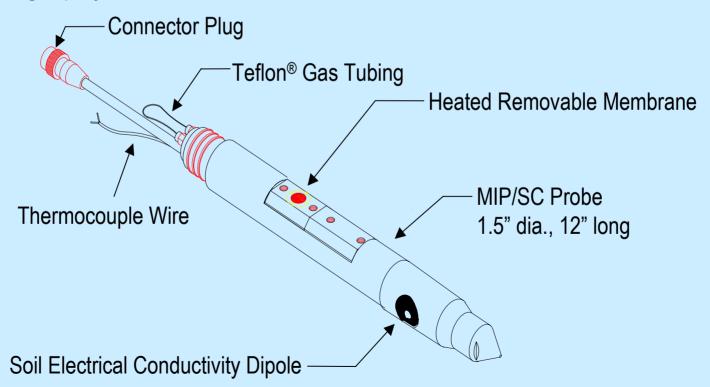
Downhole Methods

- Membrane Interface Probe (MIP)
- RNS (aka NAPL FLUTe)
- Cone Penetrometer Technology (CPT)/Laser Induced Fluorescence (LIF)
- **■** Groundwater Quality Profiling using Direct Push (DP) and Multilevel Wells
- Well Measurements for NAPL Distribution
- Characterization of NAPL Samples
- Borehole Geophysics
- Partitioning Interwell Tracer Test (PITT)
- The Future

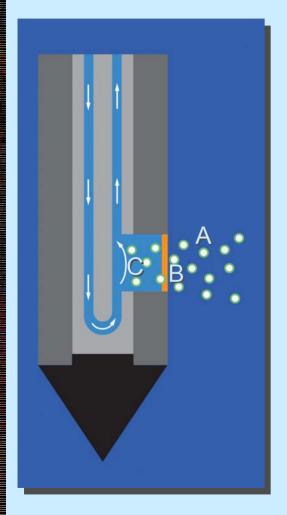


Geoprobe® Membrane Interface Probe (MIP) and Soil Conductivity (SC) System

A direct-push logging tool that records continuous relative VOC concentrations (MIP sensor) and electrical conductivity (SC sensor) with depth in soil. Provides rapid, real-time, detailed characterization of stratigraphy and VOC contamination.



MIP Theory of Operation

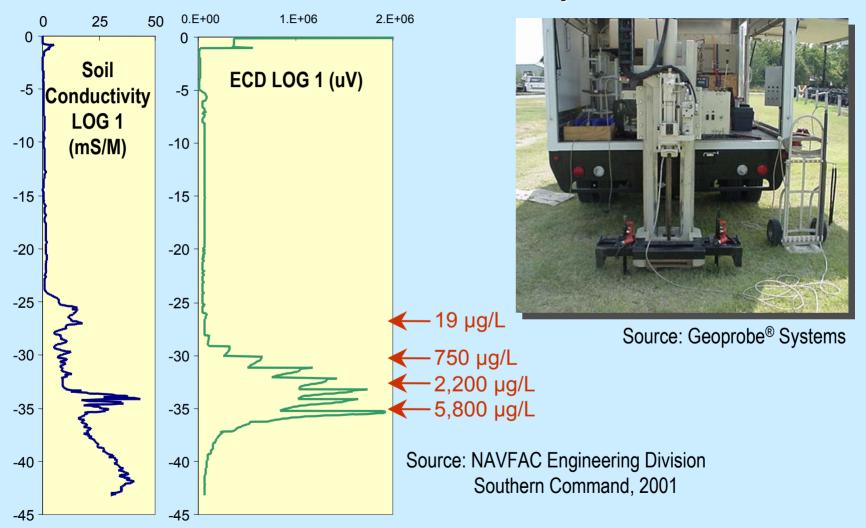


- VOCs in subsurface region (A) come into contact with a thin film Teflon® membrane (B) set in a heating block, which is heated to 120°C.
- Chemicals are volatilized and diffuse across the membrane where they are swept by an inert carrier gas (C) to various detectors at the surface.
- Continuous voltage output from VOC detectors (ECD, PID, FID) are recorded versus depth.
- Bulk fluids do not travel across the membrane; thus the MIP can be used above or below the water table.

The MIP is for VOCs

- Provides record of output voltage of the detector connected to the gas stream:
 - An electron capture detector (ECD) for chlorinated solvents
 - A photo-ionization detector (PID) for aromatic hydrocarbons
 - A flame-ionization detector (FID) for methane and petroleum hydrocarbons
- Gas samples can be analyzed by GC/MS; water and soil sampling can be guided using MIP data
- Given its <u>relatively high detection limits</u>, a good use of the MIP is to help delineate DNAPL zones

Comparing MIP and Mobile Lab GCMS Data Charleston Naval Complex



Vertical Profile of TCE via Onsite GC/MS

Membrane Interface Probe (MIP)

Advantages

- Widely available
- Simultaneous log of VOCs and soil conductivity
- Operates in vadose zone and saturated zones
- Useful for delineating NAPL source zones
- Rapid site screening (100s of feet per day)
- Cost savings

Limitations

- High detection limits, qualitative analytical data
- Designed for volatile contaminants
- Contaminant carryover can be high
- Penetration resistance limitations

Ribbon NAPL Sampler (RNS) aka NAPL FLUTe™

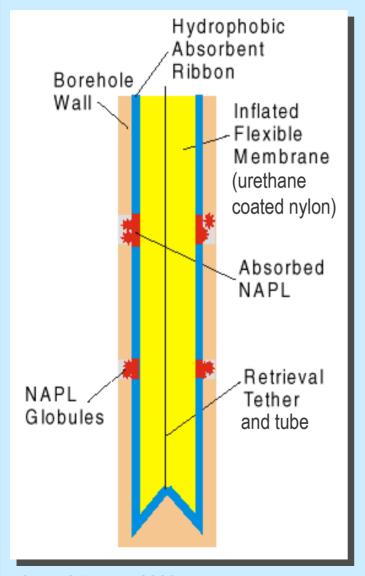
 A continuous, direct sampling method that can provide depth-discrete mapping of NAPL developed circa 1998 by Westinghouse Savannah River Co. and Flexible Liner Underground Technologies Ltd (FLUTe)



- Uses a pressurized flexible liner to support and seal a hole and force a dye-striped NAPL absorbent ribbon against a borehole wall
- More than 300 installations in ~30 states

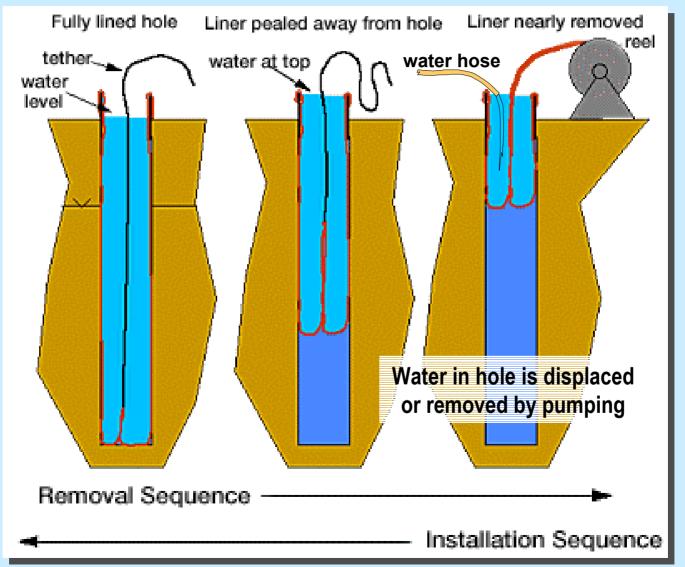


RNS Theory of Operation



- A flexible membrane with a colorreactive hydrophobic cover is installed downhole
- NAPL wicks into the cover, leaches dye from its surface, and visibly stains the white backside of the reactive material
- The liner/cover is inverted out of the hole to prevent cross contamination of the cover
- The liner is stripped from the cover to inspect the white side of the cover for stain patterns

RNS Emplacement by Eversion (inside-out) in Open Hole below Water Table "like taking a sock off"



Downhole RNS (aka NAPL FLUTe™)

Advantages

- Provides continuous record of NAPL distribution with depth at borehole location
- Can be deployed in variety of hole types
- Can provide cost savings

Limitations

- Heterogeneity may limit value of information
- Relatively ambiguous reaction to some NAPLs may be difficult to interpret
- Wicking may exaggerate NAPL presence
- Potential for false positives and false negatives
- Potential for cross contamination

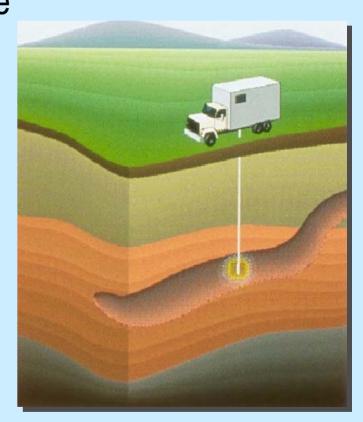
Downhole UV Fluorescence Probes Developed in 1990s

- Site Characterization and Analysis Cone Penetrometer System (SCAPS)
 - Developed by Navy, Army, Air Force, and DOE
 - ~8 SCAPS CPT-LIF units for federal government use
- Rapid Optical Screening Tool (ROST) CPT-LIF
 - Developed by Dakota Technologies, Inc. (DTI) and marketed by Fugro Geosciences, Inc. and DTI
 - Fugro operates 7 ROST systems in U.S. and Europe
 - DTI operates 1 Geoprobe® ROST unit
- The Fuel Florescence Detector (FFD), with a downhole mercury lamp
 - Developed and marketed by Applied Research Associates (ARA)
 - >20 FFD units operated by various companies in U.S.

Invasive Tools: Downhole Methods

Cone Penetrometer Technology/ Laser Induced Fluorescence (CPT/LIF)

- CPT uses strain gauges to measure soil behavior properties (tip and sleeve resistance) to provide real-time, in situ stratigraphic identification
- LIF provides real-time logging of fluorescent contaminants
- Probe continuously advanced smoothly at ~4 ft/min in accord with ASTM Standard D-3441



Source: Fugro, 1999

■ CPT rigs vary from 20 to >35 tons in truck and ATV format

LIF/FFD Applications

- Polycyclic aromatic hydrocarbons (PAHs) in petroleum products, coal tar, and creosote
- Double-ring (naphthalene) and single-ring aromatic hydrocarbons (BTEX compounds) at lower excitation wavelengths
- Chlorinated solvents (e.g., PCE, TCE) and other NAPLs mixed with fluorescent impurities can produce strong fluorescent signals
- LIF has mainly been used to delineate petroleum (at POL sites) and coal tar contamination (at wood-treating and manufactured gas plant [MGP] sites) at relatively shallow depths

CPT/LIF UV Fluorescence Probes

Advantages

- Real-time delineation of stratigraphy and fluorescent contamination
- Typical daily productivity of 300 to 400 feet at 10 to 15 locations
- LIF waveforms offer product identification/verification and rejection of non-contaminant fluorescence
- Reduced IDW and exposure to site contaminants
- Potential cost savings

Limitations

- Primarily applicable to PAHs
- Subject to interferences
- NAPL has to be adjacent to sapphire window
- Limited availability
- Cost



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Invasive Tools: Groundwater Quality Profiling Using DP and Multilevel Wells

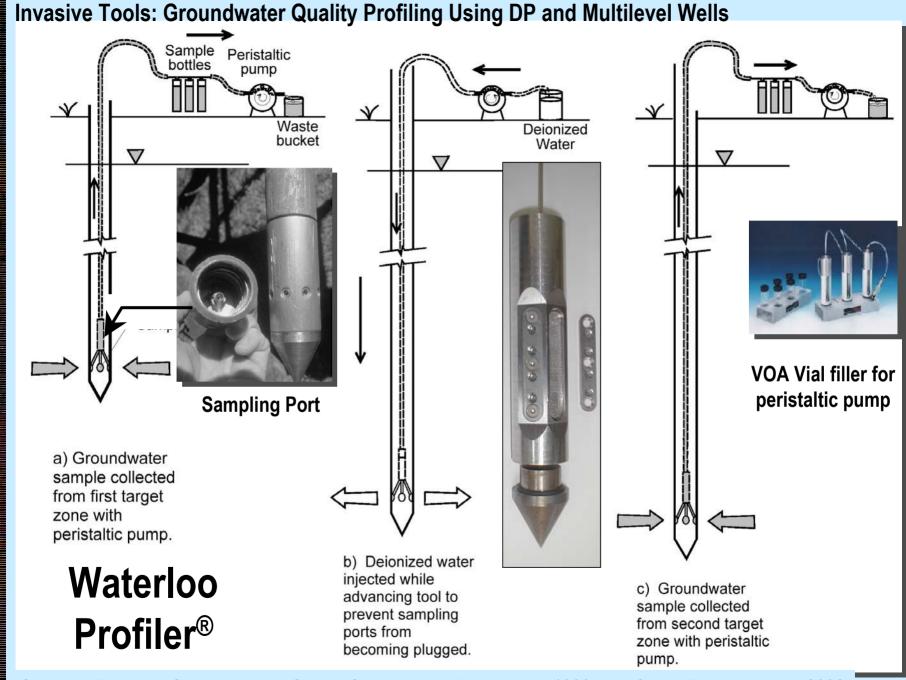
Groundwater Quality Profiling Using DP Tools

- Collect multiple discrete groundwater samples from coarse sediments at multiple depths in a single hole
 - Waterloo Profiler®
 - Geoprobe[®] Dual Tube and GW Profilers
 - VERTEK ConeSipper™
- Need to know stratigraphy to select sampling zones
 - Based on CPT log, electrical conductivity (EC) log, K-test, geologic log...
- Combine with mobile lab for real-time measurement and dynamic site
 characterization Source: Stone Environmental, Inc.



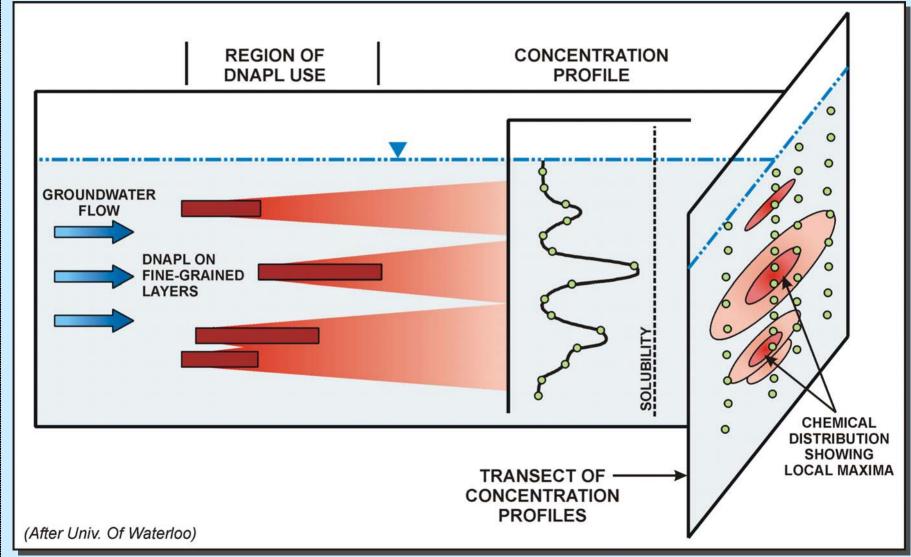
Geoprobe® DT21 Profiler





Invasive Tools: Groundwater Quality Profiling Using DP and Multilevel Wells

Using Groundwater Concentration Data to Locate DNAPL Source Zones



Advantages of DP Groundwater Profiling

- No drill cuttings and little purge water
- Can pump clean water out through screen during advancement to minimize clogging and dragdown of contaminants*
- Can collect multiple samples (at any spacing) with depth using peristaltic or pneumatic low-flow pumping methods*
- Can perform K tests*
- Can develop well screen*
- Holes can be grouted through rods
- Provides detailed concentration profiles that can be used for backtracking to DNAPL source
- Rapid and relatively cost-effective

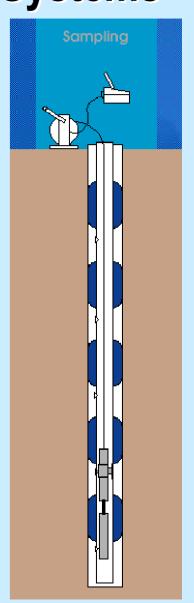
^{*} See specific products for availability

Limitations of DP Groundwater Profiling

- Limited by lithology (clogging, turbidity, and lack of yield problematic in fine-grained sediments) and depth (depending on drilling and sample collection methods)
- Only provides a snapshot in time of water quality
- Concentrations of metals and hydrophobic compounds likely to be biased due to sample turbidity
- Vertical hydraulic gradients can impact backtracking interpretation
- Due to heterogeneity and dilution effects, can still be difficult to define morphology of DNAPL sources
 - Concentration > effective solubility indicates NAPL in sample
 - Concentration < effective solubility requires interpretation

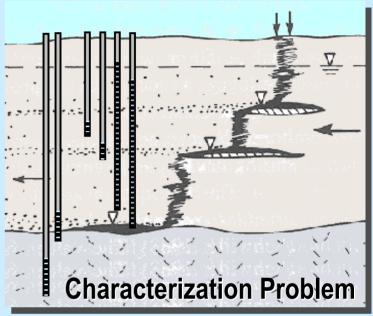
Multilevel Groundwater Monitoring Systems

- For measuring groundwater quality, hydraulic heads, and hydraulic conductivity in overburden and bedrock
 - Continuous Multichannel Tubing (CMT™) (www.solinst.com)
 - Waterloo Multilevel System (www.solinst.com)
 - Westbay MP System[®] (www.westbay.com)
 - Water FLUTe[™] (www.flut.com)
 - Conventional Methods



Interpreting Dissolved Concentrations

- Complex DNAPL distribution leads to highly stratified dissolved plume concentrations
- Although lab experiments show NAPL:Water equilibrium at 10-100 cm/d flow, groundwater concentrations at DNAPL sites are typically <1% and <10% of solubility</p>
 - Non uniform NAPL distribution
 - Mixing of groundwater in well
 - Effective solubility



Invasive Tools: Groundwater Quality Profiling Using DP and Multilevel Wells

| Compound | % Weight | FW | _ | Effective Solubility (mg/L) [S _{ei}] |
|---|-------------|-------|-------|--|
| Polycyclic Aromatic Hydrocarbons (PAHs) | 85 | | | |
| Naphthalene | 11 | 128.2 | 31.7 | 4.8 |
| 2-Methylnaphthalene | 11 | 142.2 | 25.4 | 3.5 |
| Phenanthrene | 11 | 178.2 | 1.3 | 0.14 |
| Anthracene | 11 | 178.2 | 0.07 | 0.008 |
| | 7 | 142.2 | 28.5 | 2.4 |
| 1-Methylnaphthalene | 7 | | | |
| Biphenyl | - | 154.2 | 7.5 | 0.58 |
| Fluorene | 7 | 166.2 | 2 | 0.14 |
| 2,3-Dimethylnaphthalene | 3 | 156.2 | 3 | 0.11 |
| 2,6-Dimethylnaphthalene | 3 | 156.2 | 2 | 0.076 |
| Acenaphthene | 3 | 154.2 | 3.9 | 0.15 |
| Fluoranthene | 3 | 202.3 | 0.26 | 0.008 |
| Chrysene | 2 | 228.2 | 0.002 | 0.00003 |
| Pyrene | 2 | 202.3 | 0.14 | 0.002 |
| Phenolic Compounds | 10 | | | |
| Phenol | 2 | 94.1 | 82000 | 3048 |
| o-Cresol | 1 | 108.1 | 25920 | 419 |
| m-Cresol | 1 | 108.1 | 23500 | 380 |
| p-Cresol | 1 | 108.1 | 24000 | 388 |
| Pentachlorophenol | 1 | 266.4 | 14 | 0.092 |
| N-, S-, and O- | | | | |
| Heterocyclic Compounds | 5 | | | 0002, DNADL Dot |

Major Components of Coal Tar Creosote

$$S_{ei} = X_i S_i$$

 X_i = mole fraction of i

- The mass of 1 mole of a compound equals its formula weight (FW).
- Mole fraction of component A = number of moles of A in mixture divided by the total number of moles of all components.

After Mueller et al., 1989

Invasive Tools: Groundwater Quality Profiling Using DP and Multilevel Wells

DNAPL Well Design

- Base placement (horizontal and vertical) and design of wells on careful logging and site understanding
- Avoid cross-contamination
- Complete open interval to top of capillary barrier
- Sandpack should be coarser than media
- Use competent and compatible materials

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- **■** The Future





Well Measurements for NAPL Distribution

- Provides qualitative information
- DNAPL at residual saturation will not enter well
- Compare to boring data
- Measurement devices
 - Interface probe
 - Bailers, tubes
 - Pumps
 - Bomb sampler
 - Weighted cotton string
- Collect DNAPL to determine properties





RITS Spring 2003: DNAPL Detection and Characterization Techniques

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Invasive Tools: Characterization of NAPL Samples

Why Measure NAPL Properties (if one can obtain a sample)?

- Textbook values may not be representative of impure subsurface NAPL due to:
 - Release of off-spec material, mixtures, etc.
 - Weathering
 - Contact with water and solids in the subsurface
- Need to understand NAPL properties and variability to assess migration and remedial alternatives



Chocolate syrup bottoms found in soil behind candy bar factory

Invasive Tools: Characterization of NAPL Samples

Properties of Fluid and Media

- Density*
- Viscosity*
- Interfacial Tension
- Wettability**
- Saturation
- Capillary pressure
 - Displacement pressure
 - Residual Saturation
- Relative permeability

- Composition
- Partitioning
 - Solubility
 - Sorption
 - Vaporization
 - Volatilization

*Can be measured easily and inexpensively
**Can be examined qualitatively



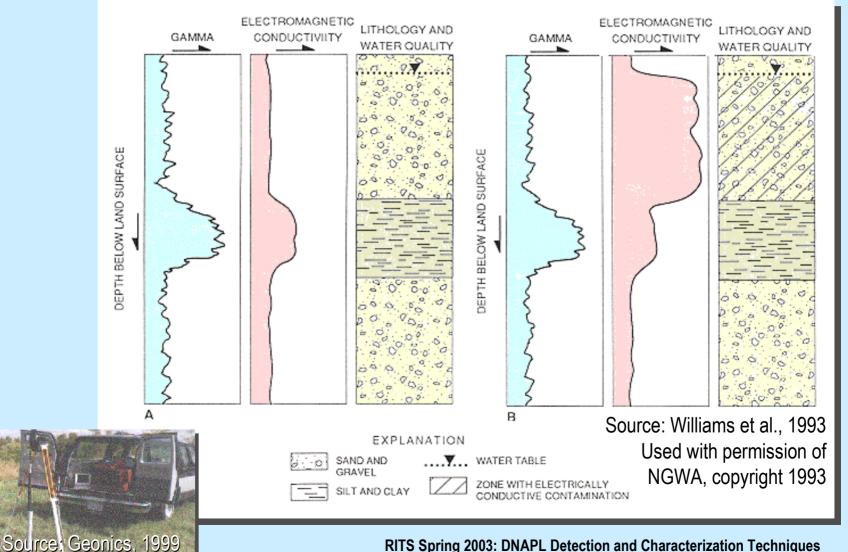


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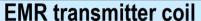
Borehole Geophysics Logging to Determine Stratigraphy



Invasive Tools: Borehole Geophysics

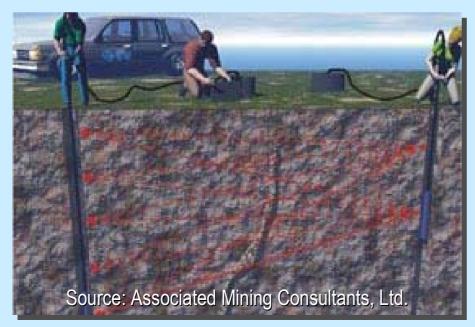
Cross-Hole and Surface-to-Hole Geophysical Imaging in Search of NAPL







Downhole receiver



- Cross-hole GPR: NAPL causes radar wave attenuation
- Cross-hole electrical resistance tomography (ERT): NAPL increases resistivity
- Surface-to-hole high-resolution electromagnetic resistivity (EMR): NAPL increases resistivity
- Cross-hole high-resolution seismic reflection: NAPL reduces P-wave velocity and amplitude
- Vertical induction profiling (surfaceto-hole): NAPL increases resistivity

Geophysical Imaging Limitations

- DNAPL is a poor geophysical target
- Interferences
- Erroneous interpretations
- Cost (may need many closely spaced holes)

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Partitioning Interwell Tracer Test (PITT)

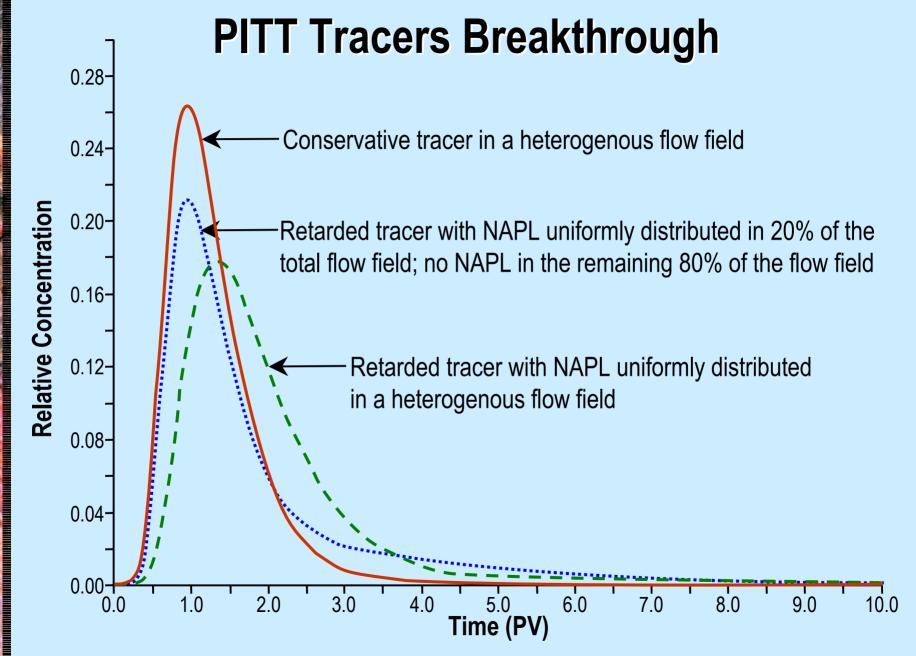
- Residual DNAPL saturation is estimated by comparing the retardation of tracers that partition into the DNAPL phase (e.g., alcohols), to tracers that are not retarded (e.g., bromide)
- Provides useful data for designing and assessing the performance of DNAPL remediation technologies
- Previous RITS topic, from Surfactant-Enhanced Aquifer
 Remediation (SEAR) for DNAPL presentation (June-July 1998)

Invasive Tools: PITT

Protocol for PITT Design and Implementation

- Characterize DNAPL zone (problematic)
- Select tracers
- Develop model of the aquifer and run simulations to complete the final design
- Install injection/extraction wells
- Conduct conservative tracer test for further refinement of flowrates (optional)
- Conduct PITT
- Data analysis (e.g., using UTCHEM)

Invasive Tools: PITT



PITT (cont.)

Advantages

Can estimate DNAPL saturation

Limitations

- Need to know DNAPL location
- Need sufficient hydraulic conductivity for tracer test
- Need small enough source to allow adequate well spacing to conduct tracer test in reasonable time frame
- The presence of natural organic carbon may cause some difficulty with the interpretation of the results
- For heterogeneous DNAPL distribution (especially pools), underestimates DNAPL volume
- Expensive and regulatory concerns may require recovery of tracers

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Invasive Tools: The Future

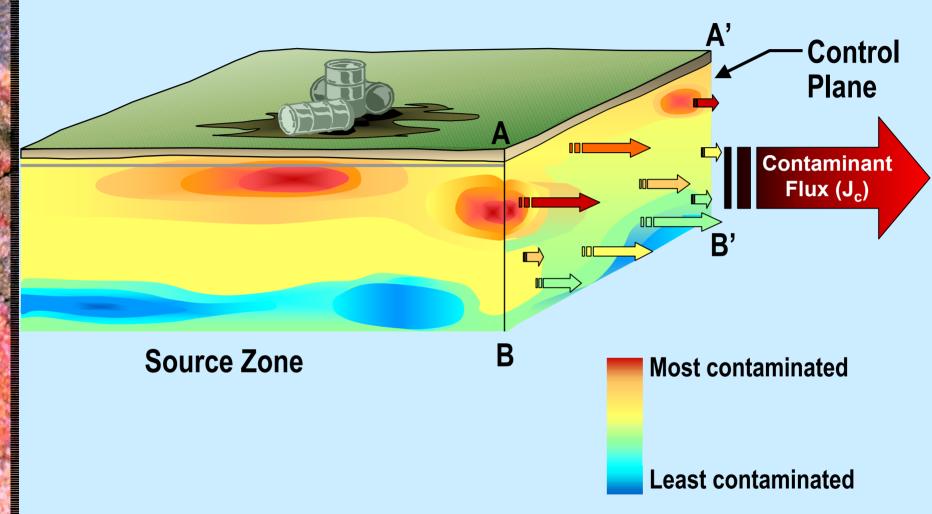
DNAPL Impact Characterization

Downgradient Contaminant Mass Flux Distribution

- A way to assess DNAPL impact to groundwater; provides estimate of DNAPL source strength and contaminant mass loading
- May become metric to assess remediation
- Key input to evaluate monitored natural attenuation

Invasive Tools: The Future

Downgradient Mass Flux



Source: Enfield, 2001

Methods to Measure Mass Flux

- Use water quality data from transects (multiple locations and depths) combined with groundwater velocity
- Use downgradient aquifer tests in a transect of wells (Bockelmann et al., 2001; Ptak and Teutsch, 2000)
- Use of sorptive permeable media placed in downgradient wells to intercept contaminated groundwater and release resident tracers (Hatfield et al., 2001)

Presentation Overview

- Definitions
- Why is DNAPL an Issue?
- Regulatory History and Status
- Strategies for Detection and Characterization
- Tools for Characterization
 - Noninvasive
 - Invasive
- Summary

If You Have...

- Dissolved conc. >1% of aqueous or effective solubility (e.g., TCE > 11,000 ppb, or PCE > 1,500 ppb)
- >1% soil concentration (>10,000 mg/kg)
- OVA exceeds 100-1,000 ppm
- Dissolved concentrations increase with depth (without other explanation)
- Concentrations increase up hydraulic gradient away from source release area
- Tailing and rebound
- Disintegrated PVC well

...You May Have DNAPL

Remember...

- Many tools are available to perform DNAPL investigations
- Each site is unique and there is no practical cookbook approach
- Even with all the tools, DNAPL detection and characterization is difficult
- Use noninvasive and minimal invasive methods first
- Use outside-in approach where downgradient dissolved plume is investigated before source area

Summary

- Develop conceptual model that focuses on stratigraphy migration pathways and traps
- Select source investigation methods that provide desired remediation data and minimize risk of mobilization
- DNAPL zone characterization will differ if remediation is containment or removal

Further Information (see handout)



Environmental Web Sites (with DNAPL content)

- Center for Public Environmental Oversight: [http://www.cpeo.org]
- DoD Environmental Security and Technology Certification program: [http://www.estcp.org]
- Federal Remediation Technologies Roundtable: [http://www.frtr.gov/]
- Ground-Water Remediation Technologies Analysis Center: [http://www.gwrtac.org/]
- Interagency DNAPL Consortium: [http://www.getf.org/dnaplguest/]
- Interstate Technology Regulatory Council: [http://www.itrcweb.org/]
- Joint Service Pollution Prevention Library: [http://p2library.nfesc.navy.mil/]
- The Environmental Technology Commercialization Center: [http://www.etc2.org/]
- University of Sheffield DNAPLs in Groundwater University: [http://www.shef.ac.uk/~dnapl/]
- USDOE Office of Environmental Management: [http://emsp.em.doe.gov/]
- USDOE Environmental Management Innovative Technology Reports: [http://apps.em.doe.gov/OST/itsrall.asp]
- USDOE Characterization, Monitoring & Sensor Technology (CMST) Program: [http://www.cmst.org]
- USDOE Environmental Management DNAPL Dynamics: [http://emt.osti.gov/cgi-bin/genresults?EMDnaplDynamics.results]
- USEPA Technology Innovation Office: [http://www.clu-in.org]
- USEPA Superfund Innovative Technology Evaluation: [http://www.epa.gov/ORD/SITE/]

<u>DNAPL Site Characterization – Methods</u>, <u>Strategies</u>, <u>and Miscellaneous</u>

- Cohen, R.M., and J.W. Mercer. 1993. DNAPL Site Evaluation, CRC Press, 369 p.: [http://www.hanford.gov/dqo/project/level5/dnaples.pdf]
- Daly, M., R.J. Fiacco, and H.J. Cho. 2002. Using borehole imaging sensors and immiscible-fluid absorbent liners to delineate residual DNAPL in fractured rock. Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press.
- Ewing, R.P., and B. Berkowitz. 1998. *A* generalized growth model for simulating initial migration of dense non-aqueous phase liquids. Water Resour. Res. 34:611-622.
- Griffin, T.W., and K.W. Watson. 2002. DNAPL site characterization A comparison of field techniques. The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA, 8p.: [http://www.hsweng.com/img/DNAPL%20Battelle.pdf]
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